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Carbocation and carbanion stability pdf download pc windows 10

Chemical methods 66. Insertion into a N---H and O---H 40. A carbocation is an ion with a positively-charged carbon atom. 6. Schmidt Rearrangement 49. Strangely enough, even halogens can help to stabilize carbocation is an ion with a positively-charged carbon atom. 6. Schmidt Rearrangement 49. Strangely enough, even halogens can help to stabilize carbocations through donation of a lone pair. The fact that atoms that we normally think of as electron-wthdrawing (nitrogen, oxygen, chlorine) can actually be electron-donor groups is probably one of the most difficult factors to wrap your head around in Org 2. This effect is tremendously important in the reactions of aromatic rings and also in enolate chemistry, where double bonds attached to donating groups (nitrogen and oxygen in particular) can be millions) of times more nucleophilic than alkenes that lack these groups. The bottom line of this post is that by understanding the factors which affect the stability of carbocations, you can gain tremendous insight into many different reactions, even though they may appear vastly different. This reaction is OCI- + H2O2 1O2 + CI- + H2O. • Carboanions are type of CH3 where the negative charge is not delocalized, due to conjugation can be distinguished from their 1H NMR spectra. These ylides are prepared by deprotonation of the corresponding sulfonium salts, which can be prepared from the reaction of wither dimethyl sulphoxide with methyl iodide. Proton abstraction from the corresponding sulfonium salts, which can be prepared from the reaction of wither dimethyl sulphoxide with methyl iodide. "onium" salt by a strong base ex) (C6H5)3P + CH3Br (C6H5)3P CH3 + Br - phosphonium salt C4H9Li ether (C6H5)3P CH2 + + LiBr S H3C H3C O + CH3Br (CH3)3S O + Br - sulfoxonium salt NaH SH3C CH3 O CH2 + H2 2. • The unpaired electron in a free radical is accommodated in a single occupied molecular orbital (SOMO). M. • As the electronwithdrawing ability of substituents bonded to the cabanion increases the stability of the ylide increases and its reactivity Stability and Reactivity 58. R OH + H + R O + H H R + HOHR1 R NH2 + H + R O + H H R + NH3 + R SH + H + R S + H H R + SH2 + 8. Parker Journal of the American Chemical Society 1993, 115 (7), 2655-2660 DOI: 10.1021/ja00060a014 Carbocation stabilities can also be expressed in terms of hydride affinity (R+ + H- -> RH). This is such a stabilizing influence that even primary carbocations - normally very unstable - are remarkably easy to form when adjacent to a double bond, so much so that they will actually participate in SN1 reactions.4. Carbocations Are Stabilized By Adjacent Atoms Bearing Lone PairsThe key stabilizing influence is a neighboring atom that donates a pair of electron-poor carbocation. R Cl R Cl + + Li Li R Li Li Cl + Mg 2+ Mg ClR 23. Bittner, E. A nitrene is a reactive intermediate and is involved in many chemical reactions. Carbones Free radicals Nitrenes and Nitrenium ions. Alkyl radical intermediates are stabilised by similar criteria as carbocations: the more stable it is. + 4) By the removal of an electron from a neutral molecule or a free radical 10. This reaction is similar to the well-known Diels-Alder reaction 67. The driving force is the formation of a strong P=O bond. Carboanions often act as a nucleophiles to react with electrophones species. Hoffman Rearrangement REARRANGEMENTS Mechanism 46. There's two answers as to why this is. Ylides A ylide or ylid is a neutral dipolar molecule containing a formally negatively charged atom (usually a carbanion) directly attached to a heteroatom (usually nitrogen, phosphorus or sulphur), with a formal positive charge and in which both atoms have full octets of electrons. THE GENERATION AND FATE OF FREE RADICALS The formation of radicals may involve breaking of covalent bonds homolytically, a process that requires significant amounts of energy. An extended thermochemical scale of carbocation stabilities in a common superacid Edward M. L. A free radical may be defined as a species that contains one or more unpaired electrons. Ion pairs are more likely in nonpolar solvents. Addition of a carbanion to a vinyl "onium" salt ex) (C6H5)3P + CH CH2 X - + CH3Li ether (C6H5)3P + CH CH2CH3 + LiX 3 SULPHUR YLIDES The most important sulphur ylides are dimethylsulfonium methylide and dimethylsulfonium methylide. Lossen Rearrangement Mechanism 48. 22. Generation of carbocation 1) Heterolytic fission of neutral species or direct ionization. carbon (electronegativity 2.5) connected to hydrogen (electronegativity 2.2) will be electron rich, and can donate some of those electrons to the neighboring carbocations. • Olmstead(1984): 21. Three Factors That Stabilize CarbocationsIf electrons were money, carbocations would be the beggars of organic chemistry. Low concentration Does not obey the Lewis octet rule with the exception of carbanioins, hence the high reactivity Often generated on chemical decomposition. It is often possible to prove the existence of this species by spectroscopic means. Often stabilization by conjugation or resonance. trapping Common Features 5. The main method of production of 102 is by photosensitization reactions. Study of these transient species not only provide detailed understanding of the potential energy surface for the specific reaction, but also find numerous applications in fields such as organic synthesis, photo-lithography, photo-crosslinking and photoaffinity labeling. Examples of reactive intermediates are carbocations, carbanions, reactive oxygen species (including hydroxyl radical), carbenes and nitrenes. H - H - H Cyclopentadienyl carbanion By resonance 28. Combination with a nucleophile R + cation act as an electrophile to react with nucleophiles. Here's some specific examples.(Advanced) References And Further ReadingA large number of papers have been written on various experimental and theoretical methods for quantitative preparation and enthalpy of rearrangement of the sec-butyl cation W. Radicals play an important role in combustion, atmospheric chemistry, polymerization, plasma chemistry, and many other chemistry, and many other chemical processes, including human physiology. PERSISTENT RADICAL Compounds are those whose longevity is due to steric crowding around the radical center and makes it Physically difficult for the radical to react with another molecule. Winstein (1949): Acylation (solvoysis) of norbornyl brosylate 18. Main carbon reactive intermediates: Carbocations and their stabilized equivalents such as oxonium ions. 21 • A carbanion is an anion in which carbon has an unshared pair of electrons and bears a negative charge usually with three substituents for a total of eight valence electrons. In other words, the neighboring carbon pays the carbocation may be free (this is more likely in polar solvents, in which it is solvated) or it may exist as an ion pair. Photodynamic Therapy (PDT) using Photofrin is performed by irradiating at 630 nm regions, because red light most easily penetrate to tissue. Carbocations are found to undergo four basic types of reaction 1) Combination with a nucleophile 2) Elimination of a proton 3) Addition to an unsaturated linkage 4) Rearrangement 15. Homolytic bond cleavage most often happens between two atoms of similar electronegativity. DETECTION OF FREE RADICALS • By using electron spin resonance (ESR) • Highly stabilized free radicals may be detected UV and visible spectroscopy. Detection of nitrenes can be detected and distinguished from singlet nitrenes, like carbenes by EPR. 31. The first organic free radical identified was triphenylmethyl radical, by Moses Gomberg (the founder of radical chemistry) in 1900. • Pyramidal - sp3 hybridised bond angle 109.28. geometery is thus tetrahedral • Has eight electrons • Stabilized by resonance or by inductive effect. . Proton abstraction from the corresponding "onium" salt by a strong base ex) (C6H5)3P + CH3Br (C6H5)3P CH3 + Br - phosphonium salt C4H9Li ether (C6H5)3P CH + + LiB S H3C H3C O + CH3Br (CH3)3S O + Br - sulfoxonium salt NaH SH3C CH3 O CH2 + H2 2. 19. 1,2-shift rearrangement A group on the adjacent Carbon migrates to the carbon with its lone pair of electrons giving an alkene. Combination with a nucleophile (that have a reactive lone pairs) 41. • If the SOMO is a high-energy orbital, the free radical shows a tendency to loose an electron. Triplet carbenes can be considered to be diradicals, and participate in stepwise radical additions. Beauchamp Journal of the American Chemical Society 1979, 101 (15), 4067-4074 DOI: 10.1021/ja00509a010 Table III in this paper has heats of formation for the basic alkyl cations (methyl, ethyl, isopropyl, and t-butyl), but in the gas phase. Singlet oxygen 1. • The C-atom in singlet carbene is sp2 - hybridized in which the spin -paired electrons occupy an sp2 orbital. Beginning in the 1920s much evidence began to accumulate implicating simple alkyl cations as intermediates in a variety of ionic reactions. Singlet carbenes generally participate in cheletropic reactions. Many reactions pass through carbocation intermediates. The stability order for radical: tertiary > secondary > primary Radicals next to functional groups, such as carbonyl, nitrile, and ether are even more stable than tertiary alkyl radicals. Examples of the most frequent NHCs and their nomenclature 43. The nitrogen atom has only 6 electrons available and is therefore considered an electrophile. The carbocations studied in this paper are all relatively stable arylcarbonium ions. Hydride affinities of carbenium ions in acetonitrile and dimethyl sulfoxide solution Jinpei Cheng, Kishan L. • If the SOMO is a low-energy orbital , it shows a tendency to accept an electron. 1. 3. 36. Stability of Carbanions Carbanions are stabilized by a field effect if there is any heteroatom (O, N or S) connected to the carbanionic carbon, provided that the hetero atom bears a positive charge in at least one important canonical form O C - R R CH3 O - R R CH3 27. 10 3) By the heterolysis charge "moves" from atom to atom. 5. In a Non-classical carbocations, the positive charge is delocalized by a double or triple bond that is not in the allylic position or by a single bond. Photofrin absorbs in the UV and in the visible region. N-heterocyclic carbenes (NHCs) NHCs are singlet carbenes. The stability of carbocations increases as we go from CH2 + R CH2 + R CH2 + CH factor governs many key reactions you meet in Org 1 - from Markovnikoff's rule, to carbocation rearrangements, through understanding the SN1 and E1 reactions.3. Carbocations Are Stabilized By Neighboring Carbon-Carbon Multiple BondsCarbocations adjacent to another carbon-carbon double or triple bond have special stability because overlap between the empty p orbital of the carbocation with the p orbitals of the π bond allows for charge to be shared between multiple atoms. Addition of a carbone to a phosphorus ylides 59. Using this, the value obtained is 14.5 ± 0.5 kcal/mol. Stabilities of carbocations in solution. 38. : 13. Krishnaswamy Faculty DOS & R in Organic Chemistry Tumkur University Tumakuru 2. + + R CH3 Cl - R CH2 - O + Br Br R O Br + Br - 24. Singlet oxygen (102) was first observed in 1924 and then defined as a more reactive form of oxygen. Packing a mere six valence electrons, these electron-deficient intermediates figure prominently in many reactions we meet in organic chemistry, such as That's a huge chunk of sophomore O-chem, right there. Being electron-deficient (and therefore unstable), formation of a carbocation is usually the rate-limiting step in these reactions. Knowing that, then think about this: what happens to the rate of the reaction when the carbocation intermediate is made more stable? 42. One of the most celebrated reactions for converting aldehydes and ketones to alkenes employs phosphorus ylides. The resulting allylic hydroperoxides can be easily converted into α,β-unsaturated carbonyl compounds and allyl alcohols Diels-Alder reaction: With acceptors such as cis dienes or aromatic hydrocarbons, 102 can react as a good dienophile. Arnett and Thomas C. The phosphorus ylide is sometimes referred to as the Wittig reagent. Reaction with electron rich systems, in which carbon- carbon double bonds have adjacent electron donating atoms (nitrogen, sulfur). •The efficient generation of a significant equilibrium concentration of a carbanion requires choice of a proper base. O CH3R + + H2OOH- O- R CH2 26. Examples: Gomberg's triphenyl-1-picrylhydrazyl (DPPH) 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) Application of TEMPO: as a radical trap, as a structural probe for biological systems in conjunction with electron spin resonance spectroscopy, as a reagent in organic synthesis, polymerization. The age-old answer that is still passed around in many introductory textbooks points to carbons (alkyl groups in particular) as being "electron-releasing" groups through inductive effects. REACTION INTERMEDIATES A reaction intermediate or an intermediate molecular entity (atom, ion, molecule..) with a lifetime appreciably longer than a molecular vibration that is formed (directly or in directly) from the reactants and reacts further to give (either directly) the products of a chemical reaction. Unstabilized ylides Preparation of unstabilized phosphorus ylides Preparation of stabilized phosphorus ylides 61. • Strongly reduced metals like Na or Li or Mg can convert alkyl halide to alkyl sodium or alkyl lithium or Grignard reagent. Houle and J. The lower surface shows that a transient species C is formed through a transition state TS-1, which yields the product D, via transition state TS-2. Hofelich Journal of the American Chemical Society 1983, 105 (9), 2889-2895 DOI: 10.1021/ja00347a060 This paper provides a table of the stability of 39 carbocations, measured calorimetrically by heat of formation (ionization in superacid from the corresponding carbinol). Carbonium Ions. Therefore, the activation energy will be lowered. What's that going to do to the rate of the reaction? Since the activation energy is lowered, the reactions. Neighboring carbon atoms.Neighboring carbon-carbon multiple bonds.Neighboring atoms with lone pairs.Why is this? • Stable carbanions do however exist although in most cases they are reactive. Since "opposite charges repel", you would be right in thinking that carbocations are stabilized by nearby electron-donating groups.Let's look at each of these in turn.2. Carbocations Are Stabilized By Neighboring Carbon Atoms. Formation of a metastable complex [A--B] ≠, known as the transition state, which is a saddle point in the PES. 51. Note here that this invariably results in forming a double bond (π bond) and the charge will move to the atom donating the electron pair. Hence this often goes by the name of "π donation". The strength of this effect varies with basicity, so nitrogen and oxygen are the most powerful π donors. NITRENES From 1,1-elimination reaction From thermolysis or photolysis of azides and isothcyanates 44. Photosensitization method and biologic effect in PDT: The most popular photosensitizer is Photofrin. Generation of singlet oxygen. • The equilibrium will favor carbanion formation only when the acidity of the carbon acid is greater than that of the conjugate acid corresponding to the base used for deprotonation. 35. 33. • A group attached to a carbon leaves without its electron pair. • A negative ion adds to a carbon-carbon double or triple bond. Singlet carbenes with unfilled p-orbital should be electrophilic. Tertiary carbocations are more stable (and form more readily) than secondary carbocations; primary carbocations are highly unstable because, while ionized higher order carbons are stabilized by hyperconjugation, unsubstituted (primary) carbons are not. J. 62. Last updated: March 27th, 2021 |Three Factors That Affect Carbocation StabilityThree main factors increase the stability of carbocations: Increasing the number of adjacent carbon atoms: methyl (least stable carbocation) < primary < secondary < tertiary (most stable carbocation)Adjacent pi bonds that allow the carbocation p-orbital to be part of a conjugated pi-system system ("delocalization through resonance")Adjacent atoms with lone pairsMore details below!Table of Contents1. Curtius Rearrangement Mechanism 47. + + Cyclopropenyl cation is stable due to aromatization 14. 57. Reactions of singlet oxygen Alder-ene reaction (Schenck reaction) In this reaction, oxygen adds to the alkyl substituted olefins to form allylic hydroperoxides with a migration of the double bond. • Trapping of carboanions with an electrophile may also show their formation of reaction. Addition of a carbene to a phosphine ex) (C6H5)3P + CCl2 (C6H5)3P + CCl2 (C6H5)3P CCl2 + + C4H10 + NaBr + ____ • Proton abstraction from the corresponding onium salt 1. Free radicals take part in radical addition and radical substitution as reactive intermediates. Well, the energy of the transition state leading to the reaction will be lower. • Shape of carbenes is planar. An Acidity Function (C0) Derived from Arylcarbonium Ion Equilibria C. Sulphur ylides react with saturated aldehydes and ketones to provide epoxides 63. 4. • NMR spectroscopy can detect free radicals (by studying the overhauser effect). 1. Ylides are thus 1,2-dipolar compounds As the electron-donating ability of substituents bonded to the heteroatom increases, the stability of the ylide increases and its reactivity decreases. NO2 3OCH > 2CH 30. For example; F CH3 CH3 SbF5 C + CH3 CH3 SbF5 C + CH3 CH3 SbF6 - 20. 14. • π- Insertion reaction also can detect and distinguish the formation of singlet and triplet. The carbocations studied in this paper are also fairly stable arylcarbonium ions, as these are measured electrochemically in either DMSO or acetonitrile. Photoelectron spectroscopy of methyl, ethyl, isopropyl, and tert-butyl radicals. Carbanions and their stabilized equivalents such as enolates. Handoo, and Vernon D. Carbenium ion (trivalent positive species) CH3, C2H5 Carbonium ion (pentavalent positive species, non classical carbocation) Carbocation 7. CH3 C H CH3 CH3 CCH3 H C CH3 H 3° 2° 1° By inductive 29. A. Several chemical methods can generate 102. Electron-donating groups destabilize it. • A carbone is a highly reactive species containing a carbon atom with six valence electrons and having the general formula RR'C:, practically all having lifetimes considerably under 1 sec. • Rotational fine structure of the UV and Visible spectra can detect the formation of the singlet (bent form) or triplet (linear form) carbones. • Triplet carbones are generally stable in the gaseous state, while singlet carbenes occur more often in aqueous media. Insertion into a C---H 39. Phosphorus ylides are divided into two categories: Stabilized Ylides PHOSPHORUS YLIDES 60. S. • Carbenes being the electrons-deficient species may take part in electrophilic aromatic substitution reactions. Olah (University of Southern California) and co-workers published the first of a series of papers describing experiments in which they could be observed by a number of spectroscopic techniques. 2) Addition of a positive species to an unsaturated system O R R + C + OH R R + CH2 CH2 + H + CH3 CH2 + O RR + CH3 F BF3 O + CH3 R R + BF4 R R O CH3 + + By the addition of a cation to a neutral molecule 9. These dioxetanes may be unstable and decompose to give carbonyl compounds Simple alkyl carbocations Stability: tertiary > secondary > primary 11. Carbocation rearrangement • Rearrangement without change in carbon skeleton 1-propyl cation reaarnged to 2-propyl cation by the migration of a hydrogen atom with its electron pair i.e 1,2-hydride shift 16. 34. The reaction is exothermic. 2. • Electron paramagnetic resonance spectroscopy(EPRS) can be used to detect the formation of the triplet carbenes. H C + H R R R R R R R R R R H + + Elimination of a proton Some carbocations act as Bronsted acid to lose a proton . In these reactions, an oxetane type adduct is formed. • Rearrangement with change in carbon skeleton Neopentyl bromide) C CH2BrMe Me Me C H2 C Me Me Me C H2 C Me Me Me -H+ C CH2OHMe Me Me X H2O 17. Saunders Journal of the American Chemical Society 1976, 98 (12), 3734-3735 DOI: 10.1021/ja00428a072 This paper describes a novel calorimetric method for measuring the heat of isomerization of the sec-butyl cation in superacid solution. Non-classical ions are a special type of carbonium ions displaying delocalization of sigma bonds in 3-center-2-electron bonds of bridged systems. Photofrin, when activated by light, undergoes a chemical reaction, which produces a cytotoxicity agent, leading to cell death. REACTION INTERMEDIATES By Dr. G. • Structure and bonding the total spin=0 Bond angle=102^o For single Methylene the total spin=1 Paramagnetic, may be observed by electron spin resonance spectroscopy 32. I. sp3 hybrid orbital containing lone pair Tetrahedral structure of carboanion 25. The numbers agree with intuition from solution-phase experiments; stability increases from methyl -> ethyl -> isopropyl -> t-butyl. Chain reactions involving free radicals can usually be divided into three distinct processes: initiation, propagation, and termination. A nitrene (R-N:) is the nitrogen analogue of a carbene. • Disintegration of diazoalkanes and their analogs, via photolytic, thermal, or transition metal (Rh, Cu)-catalyzed routes. • Formation of carbanions can be detected by the UV and Visible spectra of the different from the starting compounds. Species C is an example of a reactive intermediate. Metal catalyzed C-H insertion Mechanism 50. 54. Reactions of Carbenes and Carbenes exhibit divergent reactivity. Carbenoids (Metal stabilized carbenes) A transition metal carbene complex is an organometallic compound containing a divalent organic ligand. • Base-induced α -elimination • Carbenes are intermediates in the Wolff rearrangement. The electron density at the charge over the α carbons. It all goes back to the core governing force in chemistry: electrostatics. For eg; in Riemer -Tiemann reaction. 45. • Formation of carbocation can be detected by NMR spectroscopy as the cation formation shifts the proton signals appreciably downfield due to deshielding of protons. One of the biologically singnificant reactions is hydrogen peroxide and hypochlorite ions reaction because OCl- can be formed by the enzyme myeloperoxidase during phagocytosis. • Formally a carbanion is the conjugate base of a carbon acid. Abstraction of PDT, the cytotoxic agent is produced by one of two different processes called Type I or Type II. Another physical method is microwave or radiofrequency discharge that generates up to 10% concentration of singlet oxygen (1 Δ g) in an oxygen atmosphere. Implications for the thermochemistry and structures of the radicals and their corresponding carbonium ions A. So By Understanding How Carbocations Are Stabilized

You Can understand The Effect Of Substituents On Reaction RatesWhy is this important? : CH3 + CH3 CH2 + CH + CH3CH3 C + CH3CH3 CH2 + CH410 + NaBr + ____ • Addition of a carbene to a phosphine ex) (C6H5)3P + CCl2 (C6H5)3P +

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